[0005] Research in this area has been wide ranging, and improvements that may provide the catalysts with increased efficiency and/or an extended useful life have been sought in the areas of components of the catalyst, e.g., carriers, promoters, and catalytic species, methods of making the catalyst and even the epoxidation processes themselves. And yet, further improvement would be welcome in the art.

[0006] Desirably, methods would be provided that would be capable of producing epoxidation catalysts that exhibit an increase in efficiency relative to conventional catalysts.

SUMMARY ~~OF THE INVENTION~~

[0007] The present ~~invention~~disclosure provides methods for producing epoxidation catalysts that exhibit enhanced efficiencies relative to conventionally produced epoxidation catalysts. More specifically, the present methods provide for the selective impregnation of a catalyst support. It has now been surprisingly discovered that when at least a portion of manganese is impregnated onto a support separate from other alkali metals and/or promoters, the resulting catalyst can exhibit enhanced efficiencies, e.g., of up to 1% greater than catalysts prepared according to conventional methods.

[0008] And so~~, in a first aspect~~, a method for making an epoxidation catalyst is provided. The epoxidation catalyst comprises a support, at least one catalytic species, manganese and at least one alkali metal and/or promoter. The method comprises impregnating at least a portion of the manganese in an impregnation step separate from the at least one alkali metal and/or promoter. In some embodiments, the manganese may be impregnated onto the support in combination with at least one catalytic species, which in some embodiments may comprise silver.

[0008a] In one aspect, there is provided a method for making an epoxidation catalyst comprising a support, silver, manganese and sodium, comprising: impregnating the support with manganese prior to impregnating the support with sodium; impregnating the support with silver prior to, at the same time as or after impregnation with manganese.

[0008b] In another aspect, there is provided a method for making an epoxidation catalyst comprising a support, silver, manganese and sodium, comprising: Impregnating the support with manganese separately from sodium and exposing the catalyst in between impregnations to an elevated temperature ranging from 200ºC to 600°C.

[0009] An epoxidation catalyst prepared according to the method is also provided. The at least one alkali metal and/or promoter may comprise rhenium, sodium, cesium, lithium, sulfate or combinations of these. In certain embodiments,

composition of Catalyst 1 calculated based on silver uptake and amounts of added promoter solutions and after draining and roasting, is given in Table 2.

[0084] Catalyst 2 (inventive) is prepared with an identical target formulation as Catalyst 1, the only difference from Catalyst 1 being that the manganese promoter after complexation with $(NH_4)_2EDTA$ was added along with silver during the first Ag impregnation. All the other promoters were added during the second Ag impregnation. The final composition of Catalyst 2 calculated based on silver uptake and amounts of added promoter solutions is given in Table 2 below.

[0085] Figure 1 above shows a comparison of the performance of Catalyst 1 and Catalyst 2 in the ethylene epoxidation reaction. The catalysts were tested in ¼ inch (outer diameter) stainless steel reactor tubes (once-through operation). An amount of 0.7 g of crushed catalysts (30/50 mesh sized) are thoroughly mixed with 1:1 by weight Denstone (inert from Norton Inc, USA) of the same particle size fraction and loaded in the reactor tubes. The feed compositions are: 30 mole-% ethylene, 8 mole-% oxygen, 1.5 mole-% carbon dioxide, 0.7 mole-% ethane and various ppmv levels of ethyl chloride. The total inlet gas flow rate is adjusted to give a gas hourly space velocity of 10000 h−1 as calculated for uncrushed catalyst. Reactor pressures are about 1950 KPa-gauge. The catalysts were operated at the same feed composition and a constant temperature of 240 °C. Z* was varied by varying the ethyl chloride (ECL) concentration in the feed; the plot in Figure 1 shows the change in outlet EO concentration and oxygen efficiency with variation in Z*,. The maximum (peak) oxygen efficiency obtained with the inventive catalyst (Catalyst 2) is about 1% higher than that obtained with the comparative catalyst (Catalyst 1).

[0086] Example 2

[0087] Catalyst 3 (inventive) was prepared with an identical target formulation as Catalyst 1, the only difference from Catalyst 1 being that the sodium promoter was added to the Ag solution during the first silver impregnation. All the other promoters were added during the second Ag impregnation. The amounts of promoter solutions

added to the silver-amine-oxalate solution during the impregnation steps and the final calculated composition of the catalyst based on silver uptake and added promoter solutions is given in Table 2.

[0088] Figure 2 shows a comparison of the performance of Catalyst 1 and Catalyst 3 in the ethylene epoxidation reaction. The feed Z* was varied as described in Example 1 and the response is observed. The maximum oxygen efficiency obtained with the inventive catalyst (Catalyst 3) is 0.5-0.6% higher than that obtained with the comparative catalyst (Catalyst 1).

[0089] Example 3

[0090] Catalyst 4 (comparative) was prepared with an identical target formulation as Catalyst 1, the only difference from Catalyst 1 being that the sodium promoter as well as the manganese promoter (complexed with $(NH_4)_2EDTA$)were added to the Ag solution during the first silver impregnation. The rest of the promoters were added to the silver-amine-oxalate solution during the second Ag impregnation. The amounts of promoter solutions added to the silver-amine-oxalate solution during the impregnation steps and the final calculated composition of the catalyst based on sliver uptake and added promoter solutions is given in Table 2.

[0091] Figure 3 shows a comparison of the performance of Catalyst 1 and Catalyst 4 in the ethylene epoxidation reaction. The feed Z* was varied as described in Example 1 and the response is observed. The maximum oxygen efficiency obtained with Catalyst 4 is surprisingly 1.3% lower than that obtained for Catalyst 1.

[0092] Addition of either Mn or Na in the first Ag impregnation provides an improvement in the efficiency as illustrated in examples 1 and 2; however, as shown in example 3, addition of Mn and Na together in the first Ag impregnation is detrimental to efficiency.

[0093] Example 4

[0094] Catalyst 5 (comparative) was prepared with all the promoters being added during the second silver impregnation The amounts of promoter solutions added to the silver-amine-oxalate solution during the second impregnation and the final composition of the catalyst calculated based on the silver uptake and amounts of promoter solutions added is given in Table 2.

[0095] Catalyst 6 (inventive) was prepared with an identical target formulation as Catalyst 5, the only difference from Catalyst 5 being that the sodium promoter was added to the Ag solution during the first silver impregnation. All the other promoters were added during the second Ag impregnation. The final calculated composition of catalyst 6 is given in Table 2.

[0096] Figure 4 shows a comparison of the performance of Catalyst 5 and Catalyst 6 in the ethylene epoxidation reaction. The feed Z* was varied as described in Example 1 and the response is observed. The maximum oxygen efficiency obtained with the inventive catalyst (Catalyst 5) is 0.5-0.6% higher than that obtained with the comparative catalyst (Catalyst 5).

[0097] Example 5

[0098] Catalyst 7 (inventive) was prepared with an identical target formulation as Catalyst 1, the only difference from Catalyst 1 being that the sodium and lithium promoters were added to the Ag solution during the first silver impregnation. The other promoters were added during the second Ag impregnation. The amounts of promoter solutions added to the silver-amine-oxalate solution during the impregnation steps and the final calculated composition of catalyst 7 based on silver uptake and added promoter solutions is given in Table 2.

[0099] Figure 5 shows a comparison of the performance of Catalyst 1 and Catalyst 7 in the ethylene epoxidation reaction. The feed Z* was varied as described in Example

[00103] Figure 6 shows a comparison of the performance of Catalyst 1 and Catalyst 8 in the ethylene epoxidation reaction. The feed Z* was varied as described in Example 1 and the response is observed. The maximum oxygen efficiency obtained with Catalyst 8 is 1% higher than that obtained for Catalyst 1.

[00104] Example 7

[00105] Catalyst 9 (comparative) was prepared with Ag impregnation being carried out only once. 10.34 g of carrier pills (Support No. A) was impregnated using a solution prepared by adding 0.0541 g of CsOH solution (0.4564 g Cs/g solution), 0.0605 g of lithium acetate solution (0.023 g Li/g solution), 0.0245 g of sodium acetate solution (0.071 g Na/g solution), 0.4823 g of ammonium perrhenate solution (0.0359 g Re/g solution), 0.0212 g of ammonium sulfate solution (0.2789 g SO_4/g solution), 0.0238 g of manganous nitrate solution (0.1552 g Mn/g solution) and 0.0947 g of diammonium EDTA solution (0.4128 g EDTA/g solution) to 42.0 g of silver-amine-oxalate solution containing 18.76 wt.% Ag. The impregnation, draining and roasting steps are carried out analogously to the earlier preparations. After draining and roasting, the final catalyst weight was 12.30 g. The composition of Catalyst 9 calculated based on silver uptake and amounts of added promoter solutions was Ag: 15.94 wt%, Cs: 499 ppm, Li: 28 ppm, Na: 35 ppm, Re: 350 ppm, SO_4: 120 ppm, Mn: 75 ppm.

[00106] Catalyst 10 (inventive) was prepared with an identical formulation as Catalyst 9, the only different from Catalyst 9 being that the manganese promoter was added to the carrier before the impregnation of Ag and other promoters. The catalyst preparation consisted of the following steps. A Mn solution was prepared by adding 0.0334 g of manganous nitrate solution (0.1552 g Mn/g solution) to 30 g of deionized water.10.26 g of the carrier (Support No. A) was vacuum impregnated using the above solution, the excess solution drained and the pills roasted. Subsequently another impregnation is carried out using a solution prepared by adding 0.0503 g of CsOH solution (0.4564 g Cs/g solution), 0.0560 g of lithium

acetate solution (0.023 g Li/g solution), 0.0227 g of sodium acetate solution (0.071 g Na/g solution), 0.4477 g of ammonium perrhenate solution (0.0359 g Re/g solution), 0.0200 g of ammonium sulfate solution (0.2789 g SO_4/g solution) to 42.0 g of silver-amine-oxalate solution containing 18.76 wt.% Ag. The impregnation, draining and roasting steps are carried out analogously to the earlier preparations. After draining and roasting, the final catalyst weight was 12.23 g. The composition of Catalyst 10 calculated based on silver uptake and amounts of added promoter solutions was Ag: 16.13 wt%, Cs: 499 ppm, Li: 28 ppm, Na: 35 ppm, Re: 349 ppm, SO_4: 121 ppm, Mn: 113 ppm.

[00107] Figure 7 shows that the inventive example catalyst 10 provides 0.6 – 0.7% higher initial efficiency than the comparative catalyst 9.

[00108]

[00109] Table 2

Catalyst number

	1	2	3	4	5	6	7
1st Impregnation							
Support No.	A	A	A	A	B	B	A
Support (g)	10.30	10.20	10.31	10.15	10.25	10.53	10.04
Silver-Amine-Oxalate solution (g)	40.1	43.5	43.3	43.6	42.6	41.3	
Ag content of solution (Wt.%)	26.6	26.6	26.6	26.6	26.6	26.6	26.55
Promoter Soln. A, $Mn(NO_3)_2$ 0.1552 g Mn/g, (g)		0.0375		0.0375			
Chelating Agent, $(NH_4)_2EDTA$ 0.4128 g EDTA/g,		0.1474		0.1475			

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(g)							
Promoter Soln. B, $Na_2(O_2C_2H_3)$ 0.0710 g Na/g, (g)			0.0440	0.0430		0.0777	0.0405
Promoter Soln. C, $Li_2(O_2C_2H_3)$ 0.0230 g Li/g, (g)							0.1016
Ag loading in 1st impregnation (Wt.%)	20.20	20.66	20.55	22.13	20.87	20.01	22.60
2nd impregnation							
Weight of First dip catalyst (g)	12.90	12.86	12.98	13.04	12.96	13.16	
Silver-Amine_Oxalate solution (g)	40.7	43.5	43.5	43.6	42.1	41.3	
Promoter Soln. A, $Mn(NO_3)_2$ 0.1552 g Mn/g, (g)	0.0357		0.0374		0.0682	0.0698	0.0358
Chelating Agent, $(NH_4)_2EDTA$ 0.4128 g EDTA/g, (g)	0.1402		0.1479		0.2697	0.2734	0.1411
Promoter Soln. B, $Na_2(O_2C_2H_3)$ 0.0710 g Na/g, (g)	0.0412	0.0428			0.0836		+
Promoter Soln. C, $Li_2(O_2C_2H_3)$ 0.0230 g Li/g, (g)	0.1021	0.1069	0.1076	0.1013	0.2073	0.2104	
Promoter soln. D, CsOH 0.4564 g Cs/g, (g)	0.0982	0.1028	0.1032	0.0974	0.1616	0.1649	0.0986
Promoter soln. E, NH_4ReO_4	0.8744	0.9174	0.9210	0.8683	1.4412	1.4642	0.8780